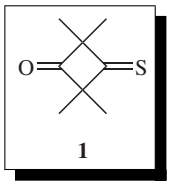
# 2,2,4,4-Tetramethylcyclobutane-1-one-3-thione

Heimgartner, Heinz ; Mlostoń, Grzegorz

# 2,2,4,4-Tetramethylcyclobutane-1-one-3-thione



**1**

*[10181-59-6]* $C_8H_{12}OS$ (MW 156.25)

(reagent used as a stable thioketone and a model for the comparison of the reactivities of strained carbonyl and thiocarbonyl groups)

*Alternate Name:* 2,2,4,4-tetramethyl-3-thioxocyclobutanone, 2,2,4,4-tetramethyl-3-thio-1,3-cyclobutanedione.

*Physical Data:* mp 57–58 °C.

*Solubility:* soluble in chlorinated hydrocarbons, hydrocarbons, ethers, alcohols, pyridine, and other commonly used organic solvents; insoluble in water.

*Form Supplied in:* red crystals, commercially not available.

*Analysis of Reagent Purity:* $^1$H-NMR, $^{13}$C-NMR, single crystal X-ray analysis.[1]

*Preparative Methods:* the title reagent can be prepared by thionation of 2,2,4,4-tetramethylcyclobutane-1,3-dione with $P_4S_{10}$ in pyridine at 110 °C.[2–4]

*Purification:* column chromatography (silica gel, hexane/dichloromethane); sublimation.

*Handling, Storage, and Precautions:* camphoraceous odor; store in a refrigerator, safe in handling.

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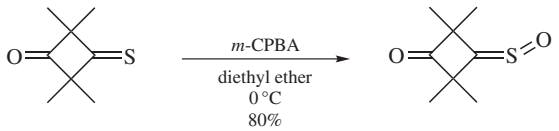
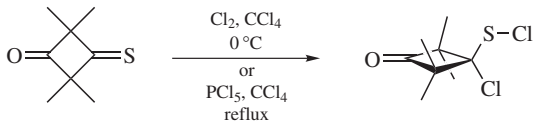
**Oxidation Reaction.** Treatment of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1**) with *m*-CPBA in diethyl ether (or dichloromethane) at 0 °C gives the colorless sulfine (thioketone *S*-oxide, **2**) in 80% yield (eq 1).[5] The same product is reported to be formed by sensitized photochemical oxidation of **1** with $O_2$/methylene blue in chloroform.[6]




**1** **2** (1)

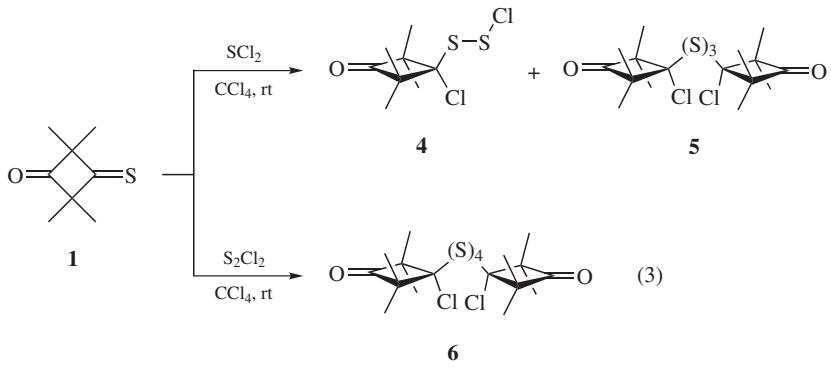
The chlorination of **1** with gaseous chlorine in tetrachloromethane at 0 °C[7] or with phosphorus pentachloride in boiling tetrachloromethane[8] affords the stable $\alpha$-chloro sulfanyl chloride (**3**) (eq 2). Phosphorus pentachloride can be replaced by sulfuryl chloride ($SO_2Cl_2$).




**1** **3** (2)

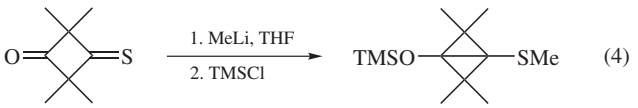
Sulfur dichloride in tetrachloromethane adds easily to **1** to give disulfanyl chloride **4** along with trisulfane **5** as a side product.[8,9]

In an analogous reaction, disulfur dichloride and **1** react slowly and tetrasulfane **6** is formed as the exclusive product (eq 3).[8]



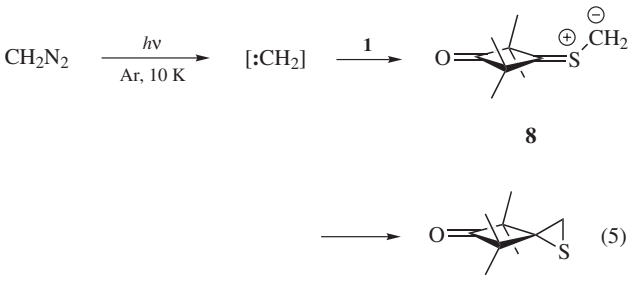

**1** **4** **5** **6** (3)

**Reactions with Organometallics.** Treatment of a mixture of **1** and alkyl bromides in THF with magnesium leads chemoselectively to 3-alkylthio-2,2,4,4-tetramethylcyclobutanones in a thiophilic addition of the in situ generated Grignard reagent.[10] The thiophilic addition is also observed with methyllithium, and quenching with TMSCl results in the formation of bicyclo[1.1.0] butane (**7**) (eq 4).[11]




**1** **7** (4)

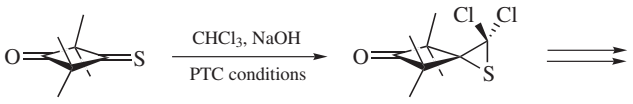
**Reactions with Carbenes and Carbenoids.** Photochemical decomposition of diazomethane in the presence of **1** in an argon matrix at 10 K yields thiocarbonyl *S*-methylide (**8**) via addition of methylene to the sulfur atom.[12] While increasing the temperature, **8** undergoes a 1,3-dipolar electrocyclization to give thiirane **9** (eq 5).



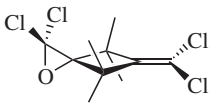

**8**

**9** (5)

Under PTC conditions, involving trichloromethane and aqueous sodium hydroxide, **1** is converted into the *gem*-dichlorothiirane (**10**), which subsequently undergoes desulfurization and, finally, the C=O group is transformed into a stable *gem*-dichlorooxirane (**11**) (eq 6).[13]



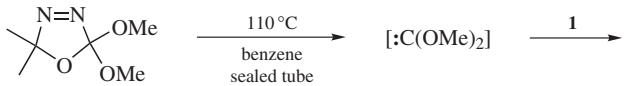

**1** **10**



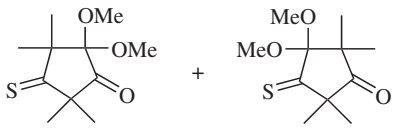

(6)

**11**

When Seyferth's reagent [(phenyl)(trichloromethyl)mercury] is decomposed in boiling benzene in the presence of **1**, 84% of thiirane **10** is obtained. Through the use of (phenyl)(trifluoromethyl)mercury and sodium iodide under the same conditions, **1** is converted in 50% yield into the difluoro analog of **10**.[14] Unexpectedly, difluorocarbene generated from bis(trifluoromethyl)cadmium in trichloromethane at $-20 \rightarrow 20\,^{\circ}C$ reacts with 2 equiv of **1** to give, in addition to the difluorothiirane derivative, 2,2-difluoro-1,3-dithiolane (a so-called Schönberg product, cf. ref 15) as the product of the interception of the intermediate thiocarbonyl *S*-difluoromethylide by **1**.[16] In contrast to halogenated carbenes, the nucleophilic dimethoxycarbene, generated by thermolysis of **12**, reacts with **1** to give the ring enlarged products **13** and **14** in favor of **13** (eq 7).[17] Remarkably, no dimethoxy thiirane derivative of **1** can be detected.



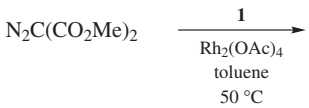

**12**

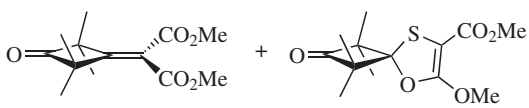



(7)

**13** **14**

The decomposition of dimethyl diazomalonate with $Rh_2(OAc)_4$ in toluene at 50 °C in the presence of **1** leads to two products **15** and **16**, which are formed via an intermediate thiocarbonyl ylide (eq 8). Whereas 1,3-dipolar electrocyclization affords a thiirane which spontaneously extrudes sulfur to give **15**, the competitive 1,5-dipolar electrocyclization yields 1,3-oxathiole **16**.[18]



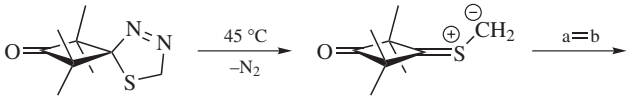

(8)

**15** **16**

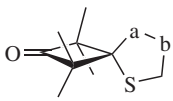
**Reactions with 1,3-Dipoles**

***Diazo Compounds***

Diazomethane reacts immediately with **1** dissolved in diethyl ether in a regioselective manner to give 2,5-dihydro-1,3,4-thiadiazole (**17**) as a relatively stable solid.[19,20] This compound is a superior precursor of the reactive thiocarbonyl *S*-methylide (**8**, eq 9) as it smoothly eliminates nitrogen at 45 °C. In the absence of an appropriate interceptor, thiirane **9** is formed.[21] In the presence of electron-deficient dipolarophiles, diverse five-membered spiro-heterocycles (**18**) are formed via 1,3-dipolar cycloaddition (eq 9).[22,23] Representative examples of dipolarophiles leading to **18** in high yield are DMAD, *N*-phenyl maleinimide, chloral, dimethyl azodicarboxylate, adamantanethione, as well as **1**.[21]



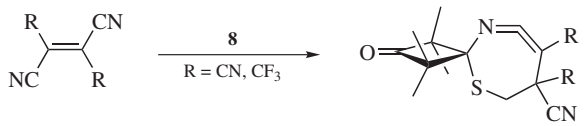

**17** **8**



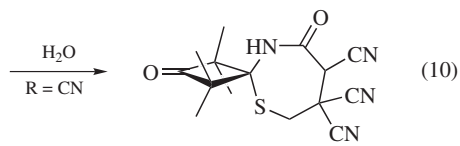

(9)

**18**

The formation of 1,3-oxathiolane with chloral and 1,3-dithiolanes with cycloaliphatic thioketones occurs regioselectively to yield the sterically less hindered products.[15] On the other hand, aromatic thioketones, e.g., thiobenzophenone or 9*H*-fluorene-9-thione, intercept **8** to give comparable amounts of both regioisomeric adducts. Usually, stereoisomeric dipolarophiles such as fumaronitrile and maleonitrile as well as dimethyl fumarate and maleate form **18** in a stereoselective manner. However, in the case of extremely electron-poor dipolarophiles, e.g., dimethyl 1,2-dicyanofumarate or (*E*)-1,2-bis(trifluoromethyl)ethylene-1,2-dicarbonitrile, non-stereospecific formations of the corresponding tetrahydrothiophenes are described.[24,25] This result is interpreted in terms of a stepwise reaction mechanism with a zwitterion as the key intermediate.[25,26] Alternatively, this intermediate can cyclize to form seven-membered ketenimines of type **20**. With R = $CF_3$, this product can be isolated in a crystalline form, whereas in the case of R = CN, stable lactam **21** is obtained only after addition of water (eq 10).



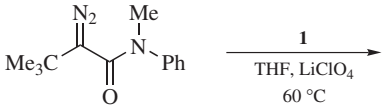

**19** **20**



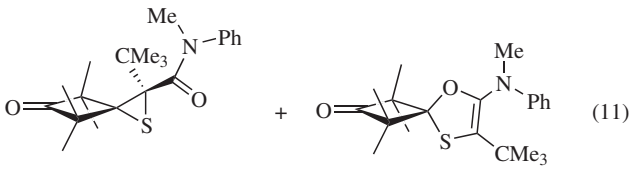

(10)

**21**

2-Diazopropane reacts with **1** at 0 °C to yield the stable 2,2-dimethyl analog of **17**, which is used as a precursor of the *S*-isopropylide of **1**.[27] The 2,2-diphenyl analog of **17**, prepared from **1** and diphenyldiazomethane, extrudes nitrogen spontaneously leading to the corresponding thiirane.[27] Similarly, EDA and **1** react at rt to give a thiirane-2-carboxylate, which can be desulfurized to yield an ethyl cyclobutylidene acetate.[28] The reactions of **1** with less reactive diazocompounds such as diazoketones, diazoamides, and diazoesters are accelerated by addition of $LiClO_4$, and thiiranes and/or 1,3-oxathioles are obtained.[28–31] Products of both types are formed in the case of $\alpha$-diazoamide (**22**) (eq 11).



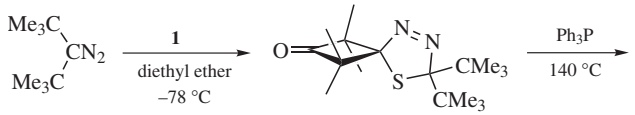

**22**



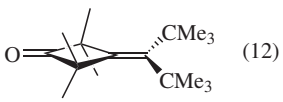

(11)

**23** **24**

With a more complex diazo compound containing amino and ester groups, products resulting from 1,3- and 1,5-dipolar electrocyclization are obtained.[32] 'Two-fold extrusion' reactions with **1** and diverse diazo compounds are reported to be aimed at the preparation of sterically crowded ethylenes.[33,34] An example with bis(*tert*-butyl)diazomethane (**25**) is shown in eq 12.




**25** **26**

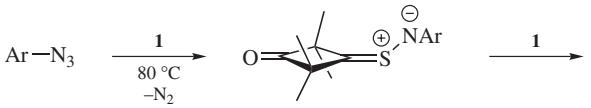



(12)

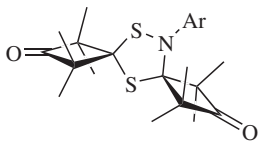
**27**

***Organic Azides***

The 1,3-dipolar cycloadditions of **1** with organic azides require elevated temperatures. Typical products of the reactions of thioketones are *N*-substituted imines, which are formed after decomposition of the initially formed 1,2,3,4-thiatriazole derivates.[35,36] However, in the case of **1** and aryl azides, the intermediate thiocarbonyl *S*-imides (**28**) intercept **1** to give dispiro-1,4,2-dithiazoles (**29**) (eq 13).[37]

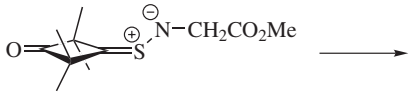



**28**

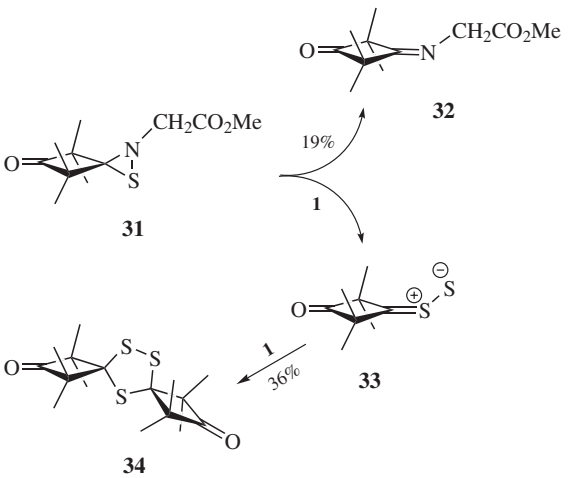



**29** (13)

The analogous reaction of **1** with benzyl azide leads to a rearrangement of the corresponding *N*-benzyl derivative of **28** via a 1,4-H shift.[38] In some cases, e.g., methyl azidoacetate, the sulfur atom extruded in the course of the reaction is intercepted by **1** to give a thiocarbonyl *S*-sulfide (thiosulfine, **33**), which subsequently undergoes a 1,3-dipolar cycloaddition with **1** yielding 1,2,4-trithiolane (**34**).[36] Thiaziridine (**31**) formed by ring-closure of **30** is a plausible sulfur donator (eq 14).




**30**

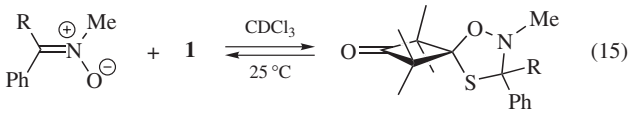



(14)

In a three-component reaction with **1** and fumaronitrile dissolved in phenyl azide, the *N*-phenyl substituted thiocarbonyl *S*-imide (**28**, Ar = Ph) cycloadds to fumaronitrile to give the corresponding 1,2-thiazolidine derivative.[32]

***Nitrones***

1,3-Dipolar cycloadditions of nitrones with **1** occur regioselectively and 1,4,2-oxathiazolidines of type **36** are obtained in high yield. Aldonitrones are more reactive than ketonitrones.[3] When stored in $CDCl_3$ solution at 25 °C, cycloreversion takes place and, in the case of **35**, the equilibrated system contains 4% of **1** with R = H and 14% with R = Ph, respectively (eq 15).[39,40]

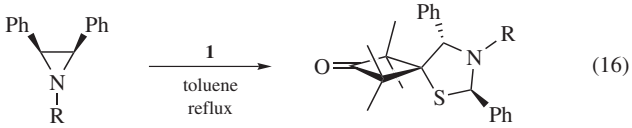



(15)

**35** **36**

***Azomethine Ylides***

Various azomethine ylides, generated by different methods, can be trapped by **1** to give spirocyclic 1,3-thiazolidines. Thermolysis of *cis*-aziridines of type **37** in the presence of **1** occurs stereoselectively to give *trans*-configured cycloadducts (**38**) (eq 16).[41] Reactions carried out with *trans*-aziridines lead to *cis*-substituted 1,3-thiazolidines.



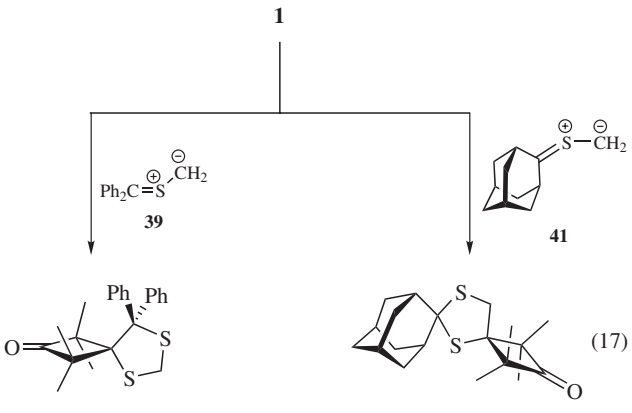

(16)

**37** **38**

Using the desilylation methodology for the generation of azomethine ylides, 2,4-unsubstituted *N*-benzyl as well as *N*-unsubstituted 1,3-thiazolidines of type **38** are prepared.[42,43]

***Thiocarbonyl Ylides***

Thiocarbonyl ylides generated by thermolysis of 2,5-dihydro-1,3,4-thiadiazoles can be intercepted by **1** to give 1,3-dithiolane derivatives (so-called Schönberg products).[44] Both aromatic and cycloaliphatic *S*-methylides undergo [2+3]-cycloadditions with **1** regioselectively. Whereas **39** yields the sterically crowded adduct **40**,[45] adamantane *S*-methylide (**41**) affords the less hindered 1,3-dithiolane (**42**) (eq 17).[46] However, the reaction of **8**, the *S*-methylide of **1**, with thiobenzophenone results in a mixture of **40** and the opposite regioisomer.[45]



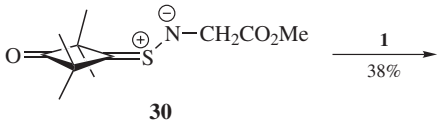

(17)

**40** **42**

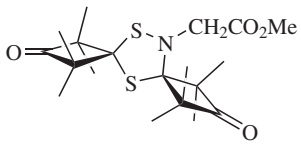
***Thiocarbonyl S-imides***

In eq 13, the interception of a thiocarbonyl *S*-imide generated in situ from **1** and organic azides is outlined.[37] Similarly, thiocarbonyl *S*-imide (**30**, eq 14) undergoes a 1,3-dipolar cycloaddition with **1** in competition with the formation of the unstable thiaziridine **31**, and the corresponding 2,5-dispiro-1,4,2-dithiazolidine (**43**) and imine **32** are obtained (eq 18).[36] A similar reaction with methyl dithiobenzoate, in which along with 1,2,4-trithiolane (**34**)

a 1,4,2-dithiazolidine of type **43** is formed, is also reported.[47]



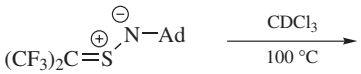

**30**




(18)

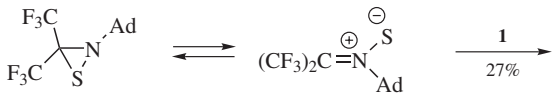
**43**

The stable, sterically crowded hexafluorothioacetone *S*-imide (**44**) reacts smoothly with aromatic thioketones, but the reaction with **1** requires elevated temperatures.[48,49] Unexpectedly, the product isolated after 3 h at 100 °C is 1,4,2-dithiazolidine (**47**). Its formation can be rationalized by the isomerization of **44** to give thiaziridine **45** being in an equilibrium with thionitrone **46**, which then traps **1** to yield **47** (eq 19).

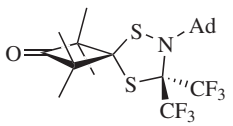



**44**

Ad = Adamantan-1-yl




**45** **46**

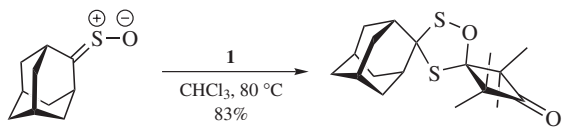



(19)

**47**

***Thiocarbonyl S-oxides (Sulfines)***

Cycloaliphatic sulfines such as **2** or **48** react with **1** in chloroform at 80 °C to give the stable 1,2,4-oxadithiolanes of type **49** in a regioselective [2+3] cycloaddition (eq 20).[50]

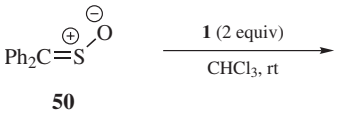



(20)

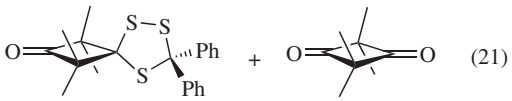
**48** **49**

In contrast, the analogous cycloadducts of aromatic sulfines and **1** cannot be isolated. Instead, 1,2,4-trithiolane (**51**) is obtained in the reaction of thiobenzophenone *S*-oxide (**50**) with 2 equiv of **1** (eq 21).[51] In this multi-step reaction, a sulfur-transfer leading to a thiocarbonyl *S*-sulfide is proposed as a key step. The formation of equimolar amounts of 2,2,4,4-tetramethylcyclobutane-1,3-dione

(**52**) indicates that in this system **1** acts as a sulfur donor. In a three-component system containing **50**, **1**, and (*E*)-cyclooctene, an episulfidation of the strained alkene is observed.[52]




**50**

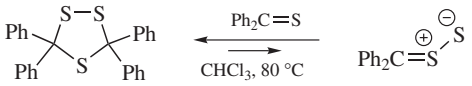



(21)

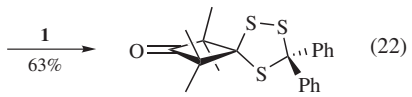
**51** **52**

***Thiocarbonyl S-sulfides (Thiosulfines)***

The formation of the symmetrical 1,2,4-trithiolane (**34**, eq 14) is the evidence for the intermediacy of thiosulfine **33** formed by a sulfur transfer from thiaziridine **31** to **1**. The mixed 1,2,4-trithiolane (**51**) (eq 22) can result either from the [2+3]-cycloaddition of thiobenzophenone *S*-sulfide (**53**) with **1** or from **33** with thiobenzophenone. Both pathways are conceivable for the formation of **51** in a three-component reaction including **1**, thiobenzophenone, and phenyl azide.[53] Tetraphenyl-1,2,4-trithiolane (**54**) undergoes a [2+3]-cycloreversion and releases **53**, which is trapped by **1** to afford **51** (eq 22). The latter is stable under the reaction conditions.[51]



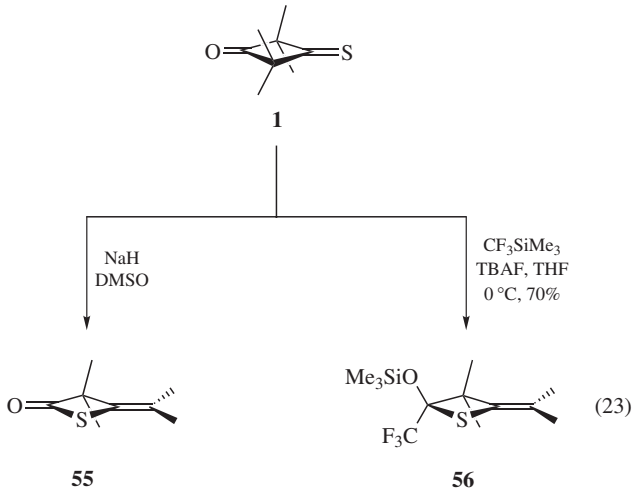

**54** **53**




(22)

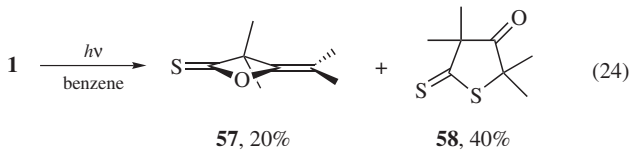
**51**

**Isomerizations.** The isomerization of **1** to thiolactone **55** occurs in DMSO solution in the presence of NaH.[2] It is reported that photolysis of **1** in methanol also affords **55**.[54] The reaction of **1** with (trifluoromethyl)trimethylsilane (Ruppert's reagent) in THF in the presence of fluoride yields the trifluoromethylated thietane **56** (eq 23).[55] A plausible mechanism of the transformation is a ring-opening/ring-closure process initiated by nucleophilic addition of trifluoromethanide to the carbonyl group of **1**.



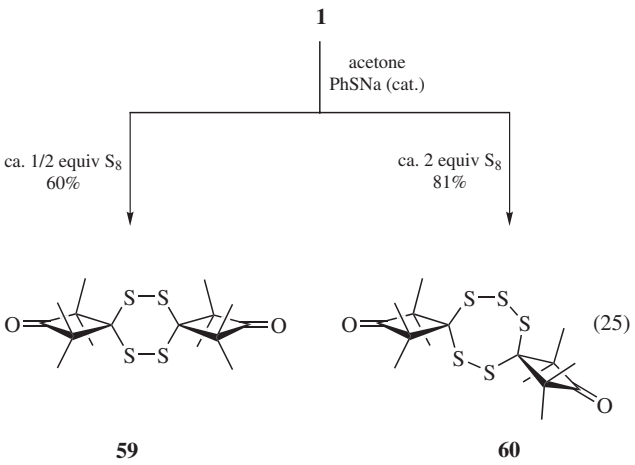

(23)

Photolysis of **1** in benzene is reported to give another isomer with the structure **57** along with the ring-enlarged 3-oxodithiolactone (**58**) (eq 24).[56]



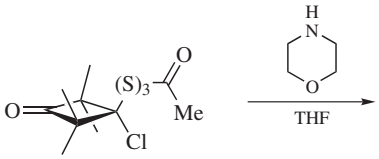

(24)

**Miscellaneous.** The sulfur-rich heterocycles **59** and **60** are produced when **1** in acetone is treated with elemental sulfur ($S_8$) in the presence of catalytic amounts of sodium thiophenolate (eq 25).[57] The type of the product depends on the ratio of **1** and $S_8$ used in the reaction.

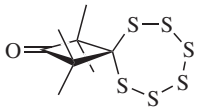



(25)

The related hexathiepane **62** can be prepared from the acetylated trisulfane **61**, obtained in two steps from **1**, by treatment with morpholine in THF solution (eq 26).[8]




**61**



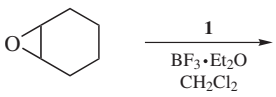
+ **60** 16%

(26)

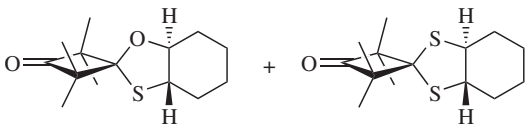
**62**

76%

Lewis acid-catalyzed reactions of **1** with oxiranes lead to 1,3-oxathiolanes and/or 1,3-dithiolanes. Whereas cyclohexene oxide (**63**) yields a mixture of **64** and **65**, only the corresponding 1,3-dithiolane is obtained in the case of cyclopentene oxide (eq 27).[58] The formation of 1,3-dithiolanes is evidenced to involve the correponding thiirane formed in situ by cleavage of the 1,3-oxathiolane ring. The structures of the products show that the heterocycle is formed with inversion of the configuration of one oxirane C-atom. This explanation is supported by the results obtained with **1** and *cis*- and *trans*-2,3-dimethyloxirane, respectively.[59] In this case, dispirocyclic 1:2 adducts are also formed by involvement of the carbonyl group of **1**.




**63**

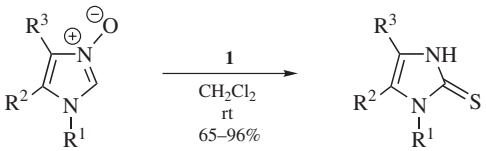


+

(27)

**64** **65**

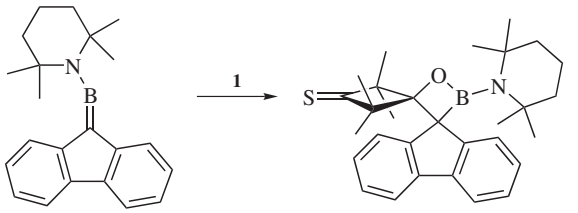
A straightforward conversion of 2-unsubstituted imidazole 3-oxides (**66**) into the corresponding imidazole-2-thiones (**67**) is achieved by the reaction with **1** in dichloromethane at rt (eq 28).[60] This sulfur-transfer reaction can be applied to other azole *N*-oxides with an unsubstituted carbon atom next to the *N*-oxide position.




(28)

**66** **67**

The reaction of amino-9-fluorenylideneborane (**68**) with **1** occurs chemo- and regioselectively at the carbonyl group to give the 1,2-oxaboretane (**69**) (eq 29).[61]




(29)

**68** **69**

The irradiation of **1** in 2-propanol in the presence of oxygen at wavelengths > 400 nm results in the desulfurization of **1** to yield the parent dione **52**. Most likely, sulfur monoxide is a side product.[2]

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